

## UTILIZATION OF COAL GASIFICATION SLAG: AN OVERVIEW

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### ABSTRACT

Coal gasification generates solid waste materials in relatively large quantities, and their disposal can represent a significant expense. For example, a 100-MW power plant based on IGCC technology using 1000 tons of 10% ash coal per day may generate over 110 tons/day of solid waste or slag, consisting of vitrified mineral matter and unburned carbon. As coal gasification technologies, considered clean and efficient methods of utilizing coal, find increasing applications for power generation, it becomes imperative that slag utilization methods be developed, tested, and commercialized in order to address the costly problems associated with its disposal as solid waste. This paper presents an overview of the experimental work that has been conducted to characterize samples of slag from various gasifiers and to identify and test a number of commercial applications for their utilization, and discusses various issues with regard to slag utilization. In the course of examining various utilization applications for a number of coal gasification slags that parallel those developed for fly ash, a better understanding of slag as a construction material has been achieved. The applications tested include the use of slag as an aggregate for road construction, cement concrete and asphalt concrete, and production of lightweight aggregate from slag.

### HISTORICAL PERSPECTIVE ON COAL WASTE UTILIZATION

In the past decade, fly ash, bottom ash, and boiler slag have increasingly been utilized in construction and other applications. In 1984, 51 million tons of fly ash was generated nationwide, of which 10 million tons, or 19.6%, was utilized in a number of applications. In Europe and Japan combustion solid wastes are utilized to a greater extent; this is attributed to the demand for construction aggregate and fill materials, the shortage of space for waste disposal, and environmental and economic factors.

The search for utilization applications for coal gasification slag parallels that of fly ash, which has been tested successfully for a variety of applications including aggregate stabilization in airport, highway, and dam construction, engineered backfill, soil amendment, cement additive, and lightweight aggregate production. A number of similar applications for gasification slag have been studied by Praxis Engineers, Inc. under a series of contracts funded primarily by the Electric Power Research Institute (EPRI) with additional support from Texaco, Inc. and Southern California Edison.

### DEVELOPMENT OF SLAG UTILIZATION TECHNOLOGY

Using fly ash utilization as a model, Praxis started work in 1986 to develop the utilization of gasification slag. The steps involved in this approach can be summarized as follows:

- o Measurement of physical and chemical properties expected to affect the utilization of slag,
- o Screening of conventional industrial and construction materials and products for potential slag utilization applications,

- o Comparison of the properties of gasification slag with the specifications established for other materials to identify possible slag substitution,
- o Testing of promising applications at the bench scale,
- o Enhancement of the properties deemed significant from the utilization viewpoint by simple, low-cost preparation techniques, and
- o Selection of successful applications for further testing at the pilot or demonstration level.

Initial testing was performed using slag samples from the Cool Water Demonstration Plant (CWDP) to demonstrate this methodology. The Cool Water plant was based on the Texaco gasification process. Sixteen potential applications for the utilization of gasification slag were initially identified based on a comparison of the preliminary characteristics of CWDP slag with those of ash by-products. The most promising of these applications included use of slag as a soil conditioner, abrasive grit, roofing granules, ingredient in cement and concrete manufacture, road construction aggregate, and lightweight aggregate. The results of this work were summarized in a paper<sup>1</sup> and presented in an EPRI report<sup>2</sup>.

Once successful utilization concepts had been identified for this slag, samples of another slag generated at CWDP from a different coal feedstock and three other slags generated from different gasifiers were also evaluated<sup>3</sup>. The three additional gasifier technologies were the Shell Coal Gasification Process, the British Gas Corporation/Lurgi Slagging Gasifier, and the Dow Entrained-Flow Gasification Process, using single-stage operation.

In a parallel study, use of slag for the production of synthetic lightweight aggregate was investigated. The findings of this study were presented in an EPRI report<sup>4</sup>. In a follow-on project, the production of lightweight aggregate from slag was successfully advanced to the pilot scale.

#### COAL GASIFICATION SLAG PROPERTIES

The physical and chemical properties of coal gasification slags were found to be related to the composition of the coal feedstock, the method of recovering the molten ash from the gasifier, and the proportion of devolatilized carbon particles (char) discharged with the slag. The rapid water-quench method of cooling the molten slag inhibits recrystallization, and results in the formation of a granular, amorphous material. Some of the differences in the properties of the slag samples that were characterized may be attributed to the specific design and operating conditions prevailing in the gasifiers. For instance, the British Gas/Lurgi gasifier produced a slag with a distinct iron-rich phase in addition to the silicate phase, and the Texaco gasifier generated slag containing a higher proportion of discrete char particles.

In general, slag is nominally in the 5-mm x 0.3-mm size range, which is equivalent to the classification for fine aggregates used in cement concrete and asphalt concrete. The apparent specific gravity of slag ranges between 2.64 and 2.81, and its dry compacted unit weight is between 70.1 and 104.9 lb/ft<sup>3</sup>. The water absorption capacity of slag varies from 2 to 16% and increases with its char content.

The elemental composition of the slag samples with respect to both major and trace elements is similar to that of the gasifier feed coal ash, as shown in Table 1. The major constituents of most coal ashes are silica, alumina, calcium, and iron. Slag fluxing agents, when used to control molten ash viscosity inside the gasifier, can result in an enrichment of calcium in the slag.

The Cool Water slag was classified as nonhazardous under the RCRA regulations. EP toxicity and ASTM extraction tests were run on a number of slags to evaluate their leachability. The slags appear to be nonleachable with respect to RCRA-listed metals. Tests for eight common anions were run, with only sulfate anions being detected at significant concentrations (25 to 200 mg/l).

#### EVALUATION OF POTENTIAL UTILIZATION CONCEPTS

Selection of applications to utilize gasification slag must take into account the fact that it is in competition with conventionally used materials whose acceptability has been established over long periods. In this effort, the emphasis was placed on evaluating the functional requirements of various applications (such as compressive strength in the case of cement concrete) in order that existing specifications--written for natural materials--do not rule out slag utilization. Ultimately, if slag is found to satisfy the functional requirements of an application, suitable standards can be established for its use in particular cases. A precedent for this procedure is the creation of a standard such as ASTM C 989-87a which was adopted for utilization of ground blast-furnace slag as cement.

Selection of the specific utilization concepts was guided by the following criteria:

- o Similarity between the properties of slag and those of the material it replaces, and
- o Achievement of comparable final products meeting the necessary functional requirements.

Based on these criteria, a number of utilization concepts were identified. These include:

Agriculture:	Soil conditioner, lime substitute, low analysis fertilizer, carrier for insecticides
Industrial material:	Abrasive grit, catalyst and adsorbent, roofing granules, industrial filler, mineral (slag) wool production, filter media
Cement and concrete:	Concrete aggregate, mortar/grouting material, pozzolanic admixture, raw material for portland cement production, masonry unit production
Road construction and maintenance:	De-icing grit, fine aggregate for bituminous pavement, base aggregate, subbase aggregate, seal-coat aggregate
Synthetic aggregate:	Lightweight construction aggregate, landscaping material, sand substitute
Landfill and soil stabilization:	Soil conditioner to improve stability, structural fill, embankment material
Resource recovery:	Source of carbon, magnetite, iron, aluminum, and other metals

Of these, a number of high-volume applications were tested at the laboratory scale and found to be suitable. For example, the potential for using slag as a fine aggregate for base, subbase, and

backfill applications is suggested by the slag size gradation. Shear strength, permeability, and compaction test data also indicate that slag would perform well as an aggregate fill material. While these applications would consume large quantities of slag they provide few economic incentives to the industry to replace cheap and abundant conventional materials with slag at this stage. However, as concern about the environment increases and recycling of waste products becomes a priority, this situation could change rapidly.

#### USE OF SLAG IN ROAD CONSTRUCTION

The use of slag in road construction was studied by testing various asphalt mix designs incorporating slag. By itself, the slag was not found to be suitable for surface pavement applications due to the lack of coarse particles and the tendency to degrade when abraded. However, its use as a subbase and base material in road construction is quite feasible as it meets a number of requirements for resistance values, e.g., the California Department of Transportation standards for Class 1, Class 2, and Class 3 subbases, and Class 2 aggregate base. To compensate for the high proportion of fine material in the slag, it may need to be mixed with a coarser material for use in specification base material and as an asphalt concrete aggregate.

Asphalt concrete hot mixes containing varying concentrations of asphalt and 30-50% slag by weight as the fine aggregate were tested for their strength (S-values) in a laboratory. A mix in which 30% slag was combined with 6% asphalt yielded an S-value of 50, which is much higher than the minimum value of 30-37 required for various grades of asphalt concrete. This mix, which had good workability, compares favorably with the standard test mix containing 5% asphalt, with an S-value of 58.

#### USE OF SLAG IN CEMENT AND CONCRETE

The composition of the slag and its natural pozzolanic properties are similar to the raw material used to make portland cement clinker. In this application, the slag carbon (char) content may be beneficial and may provide some of the fuel needed to make the clinker. The slag could also be added to cement clinker and ground with it.

The carbon content of some of the slags is far higher than the 1% limit placed on aggregate. This makes it necessary to recover the unburnt carbon from the slag, both in order to meet the standard for aggregate and to improve the process economics. Char removal was accomplished by means of simple specific gravity devices. The recovered char is a usable by-product.

Several batches of concrete were prepared using slag to replace varying quantities of the sand in the mix. Specimens in which 50% and 75% of the sand was replaced by slag had compression strengths of 2786 and 2483 psi respectively, over a 28-day curing period. This compared well with the control sample containing no slag, which had a compression strength of 3407 psi. These results indicate that slag could be used to replace a large proportion of the fine aggregate in making light-duty nonstructural concrete.

Tests to replace some of the fine aggregate used to make concrete with slag were performed by substituting 50% of the sand by slag. The test specimens achieved satisfactory results, with compressive strengths ranging from 3000 to 3500 psi, compared with a control strength of 3900 psi at the same cement content. These results satisfy typical compressive strength requirements of 2000 psi for concrete pads for sidewalks, driveways, and similar applications.

Another series of tests involved using slag ground to a fine powder as a cement replacement. Cement additive requirements have been established for blended cements in ASTM C 595 which covers five classes of blended hydraulic cements made from conventional materials for both general and specific applications. Following initial exploratory tests, it was concluded that it was necessary

to process the slag samples to remove potentially deleterious substances. The lighter char fraction was removed from one of the slags by density separation, and an iron phase was recovered from another slag by magnetic separation. The percentages of cement replaced by slag in these tests was 15% and 25% respectively. The use of processed slags resulted in a more successful replacement of cement by slag. All of the 15% slag-cement blend samples exceeded the 3-, 7-, and 28-day strength requirements of 1800, 2800, and 3500 psi respectively, and one of the four slags tested exceeded these requirements at the 25% replacement level. The other three 25% replacement level slag samples achieved the required 28-day strength but did not satisfy the 3- and 7- day requirements. The average 28-day strength for the 15% blend was 5600 psi, and that of the 25% blend was 4900 psi.

The success of the prepared slag-cement blends in achieving long-term compressive strength suggested that the ground slag would also qualify as a pozzolanic mineral admixture. A pozzolan is a finely ground siliceous material which can react with calcium ions, in the presence of water and at room temperature, to form strength-producing calcium silicate minerals in a manner similar to cement reactions. A 35% replacement of cement by slag was evaluated in accordance with the procedures outlined in ASTM C 311. The success of a pozzolanic test is measured by the Pozzolanic Index, which indicates the ratio of the sample's compressive strength to that of an ordinary portland cement control sample. All of the concrete samples thus produced exceeded the Pozzolanic Index requirement of 75%, with index values ranging between 90 and 118%.

#### SLAG LIGHTWEIGHT AGGREGATE

Lightweight aggregates (LWA) have unit weights that are approximately 40-60% those of standard aggregates. Annual consumption of LWA in the United States for various applications is approximately 15 million tons. Major applications of LWA are in the production of lightweight structural concrete used in highrise buildings and lightweight precast products such as roofing tiles, masonry blocks, utility vaults, cement concrete pipes, etc. Conventional LWAs are produced by pyroprocessing of naturally occurring expandable shales or clays at temperatures ranging between 1880 and 2200°F after pulverizing, working into a paste, and extruding them to produce pellets of the desired size. The strength requirements for lightweight concretes made from LWA are given in Table 2.

Slag-based lightweight aggregates (SLA) were produced by duplicating the processing methods used for commercial LWA manufacture. These steps included grinding the slag, mixing it with a clay binder and water, and extruding it to form long strands that were cut to the desired sizes. These wet green pellets were then dried and fired in a laboratory muffle furnace at 1800°F for 4 minutes. A unit weight of 45 lb/ft<sup>3</sup> was measured for the SLA, which is below the minimum coarse LWA specification of 55 lb/ft<sup>3</sup>. Concrete made from the SLA had a 28-day compressive strength of 3100 psi and a unit weight of 105 psi, which exceeds the ASTM requirements shown in Table 2.

Further tests have confirmed that the density of the SLA can be controlled as a function of the firing temperature, as shown in Figure 1. This indicates that SLA products can be produced to meet specific density requirements such as those for cement concrete LWA, lightweight concrete masonry units, or ultra-lightweight material used in insulating concrete.

Tests on discrete 2-mm particles of each slag showed that they also expand to form a lightweight material when fired at 1600-1900°F. Further tests on all particles larger than 0.3 mm, without pelletization, confirmed this phenomenon. The materials resulting from these tests had unit weight values of 15-25 lb/ft<sup>3</sup>. The concrete produced from one of the expanded slag samples had a unit weight of 33 lb/ft<sup>3</sup>, which qualifies it to be classified as an insulating concrete. However, it had a compressive strength of only 125 psi which is somewhat lower than the strength of commercially available insulating concretes at 200-250 psi. It is expected that the strength can be considerably

increased with minor adjustments to aggregate gradation and the cement proportions used to formulate these test samples.

The experimental work on slag utilization has been developed to the continuous pilot scale for the production of SLA from slag. The results from this test program have been very encouraging and have confirmed the bench-scale test results. During the tests, engineering information on energy requirements, scale-up information, and off-gas analysis was obtained, and the mechanism of slag expansion was investigated. The energy requirements for SLA production are considerably lower than those for conventional LWA production due to the lower kiln temperatures required for slag. Samples of the SLA generated during the pilot tests are undergoing extensive testing.

## CONCLUSIONS

Gasification slag has been determined to be an environmentally nonhazardous material, whose unique properties may be attributed to the composition of the mineral matter in the coal feedstock and the method of quench-cooling applied in the gasifier. Bench-scale test data have shown that there are a number of promising applications for the utilization of gasification slags. In particular, the utilization of slag in applications such as road and construction aggregates, cement additives, and lightweight aggregates has been demonstrated. Production of slag-based LWA (or SLA) is feasible and should be established as a priority. The high unit price of LWAs will permit SLA to be transported for greater distances while remaining economically competitive, thus rendering slag utilization less sensitive to the location of the gasifier.

## FUTURE OF SLAG UTILIZATION

Currently, in most utilization scenarios, gasification slag would be used as a replacement for materials that have a relatively low unit cost, such as road aggregates. Unless potential commercial users of slag are provided with extensive characterization and utilization data, the economic incentives alone are unlikely to be sufficient to cause them to incorporate slag into their production scenarios. The initial resistance to the use of new materials that may be encountered in the construction materials manufacturing industry can be addressed in two ways. First, the slag producer can supply complete engineering data on slag utilization to the prospective end user, who would then be responsible for any processing steps that might be required for a particular application. An alternative, more comprehensive approach would be for the slag producer to deliver the slag to the end user in a form that meets the user's specifications; these specifications could vary depending on the market demand in the vicinity of the gasifier. If recent legislation in California can be used to gain an insight into coming regulatory trends, at least 50% of the slag produced in the state will be required to be utilized in the coming decade, thereby creating additional incentives for producers and prospective end users to work together to realize its utilization potential.

## REFERENCES

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Table 1

COMPARATIVE COMPOSITION OF TYPICAL BLAST-FURNACE SLAG, COOL WATER FEED (UTAH) COAL ASH, AND COOL WATER SLAG

<u>Mineral</u>	<u>Blast Furnace Slag</u>	<u>Cool Water (Utah)</u>	
		<u>Coal Ash</u>	<u>Cool Water Slag</u>
SiO <sub>2</sub>	32-42	48.0	40-55
Al <sub>2</sub> O <sub>3</sub>	7-16	11.5	10-15
CaO	32-45	25.0	10-15
MgO	5-15	4.0	2-5
Fe <sub>2</sub> O <sub>3</sub>	0.1-1.5	7.0	5-10
MnO	0.2-1.0	NA	NA
S	1.0-2.0	NA	<1

Table 2

UNIT WEIGHT, MINIMUM COMPRESSIVE STRENGTH, AND TENSILE STRENGTH (28-Day Requirements for Structural Concrete, ASTM C 330)

<u>100% LWA mix</u>		<u>Sand/LWA Mix</u>	
<u>Unit Weight</u> <u>lb/ft<sup>3</sup></u>	<u>Compressive</u> <u>Strength, psi</u>	<u>Unit Weight</u> <u>lb/ft<sup>3</sup></u>	<u>Compressive</u> <u>Strength, psi</u>
115	--	115	4000
110	4000	110	3000
105	3000	105	2500
100	2500	100	--

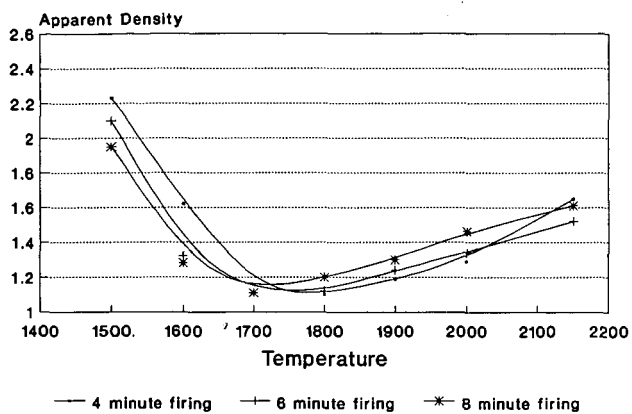


Figure 1. Time/Temperature/Density Relationship for Expansion of Slag Pellets